SYMPOSIUM ON GEOCHEMISTRY AND CHEMISTRY OF OIL SHALE
PRESENTED BEFORE THE DIVISIONS OF FUEL CHEMISTRY, GEOCHEMISTRY
AND PETROLEUM CHEMISTRY, INC.
AMERICAN CHEMICAL SOCIETY
SEATTLE MEETING, MARCH 20-25, 1983

HIGH-PRESSURE PYROLYSIS OF COLORADO OIL SHALE

By

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INTRODUCTION

Studies of pyrolysis of kerogen-rich rocks under pressure are valuable for evaluating potential oil shale processing schemes (1-5) as well as understanding the formation of petroleum (6, 7). The great variety of experimental techniques has led to a variety of results. None of the existing studies are sufficiently broad ranged to properly separate the effects of temperature (or heating rate), pressure, residence time and gas atmosphere on oil yield and composition.

In the work we present here, we have pyrolyzed Green River oil shale in a low porosity reactor where the products are allowed to escape as produced. This self-purging design results in the pyrolysis occurring in a nearly autogenous atmosphere. One application of pyrolysis results for the conditions considered here is the estimation of oil yield from radio-frequency in-situ processing (8). This report is a preliminary analysis of work in progress.

EXPERIMENTAL

The sample used in the study was a 94 L/Mg (22.4 gal/ton) Green River oil shale from the Anvil Points mine near Rifle, CO. The particle size was 0.42 to 0.84 mm (-20 +40 mesh). It contained by weight 10.88% org C, 4.76% min C, 1.64% H, 0.42% N and 0.59% S. It was a byproduct of a large-scale sample preparation for other experiments and, thereby, represents an average composition over a broad stratigraphic section of the Mahogany zone.

The apparatus used is shown schematically in Figure 1. The sample is compressed into 3.2 cm diam. pellets using a pressure of 24,000 psi. Two of these pellets, weighing a total of about 110 g, are welded into the sample can (3.3 cm diam.) along with quartz sand above and around the pellets to reduce porosity. We determined the porosity of the pellets to be about 24% from the helium buoyancy density of the raw shale and the weight and dimensions of the pellets. Total porosity in the reactor averaged 29%, or equivalently, the total void volume was about 20 cm^3.

For the near-atmospheric pressure experiments, a thermocouple in a well measured the temperature near the center of the oil shale sample. Previous experience in similar experiments indicates that the difference in temperature across the sample is less than 5°C. A second thermocouple measured the temperature outside the reactor near the furnace wall. For the high-pressure experiments, the sample thermocouple was omitted and the sample temperature was estimated from the furnace thermocouple and the difference between the sample and furnace thermocouples in the atmospheric-pressure experiments.

The sample and oil collection system is prepressurized with argon and the pressure is maintained approximately constant during the experiment by a back-pressure regulator. In fact, the pressure in the reactor increased by nearly 1 atm over the course of the experiment as the gas collection system filled. Sufficient steam is produced at temperatures below 250°C to purge the argon from the reactor. We believe that the diffusion of argon back into the reactor is sufficiently slow that the pyrolysis occurs in an atmosphere close to the composition of the pyrolysis products. At the end of the experiment, all the gas in the system is pumped into the gas collection bottle by a bellows pump. The second trap is cooled to -77°C during pumping. Other analytical procedures are the same as those described previously (9).

RESULTS AND DISCUSSION

The material balance, oil yields and distribution of organic carbon are shown in Table I. Oil properties are given in Table II. A few observations are in order. The density of the oil changes sufficiently that the yield depends strongly on whether it is calculated on a weight or volume basis, so comparisons of yields under various conditions should be made cautiously.

At near-atmospheric pressure, the oil yield decreases with a decrease in heating rate.

The volumetric yields are in excellent agreement with those previously reported by Campbell (10, 11). The slow-heating-rate oils have a lower nitrogen content due to coking of nitrogen-rich aromatics. Nearly four times as much organic carbon is converted to coke as to gas during coking reactions and the principal gaseous products are H_2 and CH_4 (Table III). Both these results are consistent with those of Campbell et al. (10). The slow-heating-rate oil has lower density and nitrogen content, in agreement with Stout et al. (12) and a lower boiling-point distribution, in agreement with Jackson et al. (13).

TABLE I

PRODUCT DISTRIBUTION

Heating rate (°C/h)	Pressure (atm)	Mass balance (%)[a]	Condensed Oil Yield		Organic Carbon Distribution[b]				
			Wt % FA	Vol % FA	Condensed Oil	Total Oil[c]	Gas[d]	Shale[e]	Total
720	1.0	99.56	100	100	65.0	66.4	5.9	22.7	95.0
110	1.5	99.73	97	98	63.5	64.6	6.1	25.2	95.9
11	1.5	99.29	86	89	56.1	57.5	7.6	29.0	94.2
1	1.5	99.18	77	81	49.6	51.0	6.2	31.9	89.0
108	27	99.34	78	84	50.3	50.5	9.1	31.5	91.1
9	27	99.41	73	80	46.3	46.4	8.6	35.4	90.4
1	26	99.36	72	79	45.7	45.9	6.6	33.8	86.2

a. Oil + water + gas + retorted shale/raw shale; sample size ~110 g.
b. Percent of the raw shale organic carbon in products.
c. Includes C_5+ compounds in gas.
d. CO, CO_2 and C_1-C_4 hydrocarbons.
e. Includes a very minor contribution from coke deposited in the sand surrounding the cores.

TABLE II

OIL PROPERTIES

Heating rate (°C/h)	Pressure (atm)	Density (g/cm^3)[a]	Elemental Analysis (Wt %)				Simulated Distillation[b]				
			C	H	N	S	10%	25%	50%	75%	90%
720	1.0	0.906	83.3	11.2	2.7	0.66	175	258	361	450	504
110	1.5	0.888	84.0	11.2	2.8	0.69	155	238	340	429	485
11	1.5	0.872	83.9	11.6	2.3	0.70	151	226	319	403	459
1	1.5	0.862	82.6	12.3	1.6	0.56	155	225	303	381	440
108	27	0.842	82.4	11.4	2.6	0.57	104	168	250	332	403
9	27	0.823	81.5	11.7	2.2	0.43	111	169	241	317	385
1	26	0.826	81.6	12.9	1.5	0.36	122	178	256	330	395

a. 23°C
b. Temperature (°C) at which the given percentage has distilled - ASTM-D-2887.

The yields from all the pyrolysis experiments at 27 atm are lower than the lowest oil yield from the atmospheric pressure experiments. The oil yield at 27 atm also decreases with a decrease in heating rate, but the effect is much smaller than at atmospheric pressure. As in the case of yield loss caused by slow heating, most of the yield loss caused by high pressure goes into coke production. This conclusion must be qualified with the caution that the carbon balances on the high pressure experiments are significantly lower than what we normally consider satisfactory. We are not sure of the reason for this problem, but the most likely source of loss is in gas, especially light hydrocarbons. Besides the possibility of leakage, which we were not able to detect, gas collection is complicated by the high gas solubility in the oil at 27 atm. About 1.5 cm^3 of "liquid" boils away when the pressure is released at the end of an experiment. The original plan was to pump the oil collection system down to several Torr, in which case C_3 and C_4 hydrocarbons would be transferred to the gas collection bottle, while C_5 and higher compounds would be captured in the dry ice trap if pumped from the oil receiver. Unfortunately, the bellows pump only reached a pressure of about 200 Torr, in which case most of the butane and some of the propane was probably retained in the dry ice trap, then lost during warmup and before weighing. This would not have been

a problem during the atmospheric pressure experiments because most of the C_3 and C_4 hydrocarbons would already be in the gas collection system prior to cooling the trap.

TABLE III

GAS PRODUCTION

(M Moles of Product/g of Raw Shale Organic Carbon)

Heating rate (°C/h)	Pressure (atm)	H_2	CH_4	C_2H_x	$\frac{C_2H_4}{C_2H_6}$	C_3H_y	$\frac{C_3H_6}{C_3H_8}$	C_4H_z
720	1.0	1.47	0.98	0.47	0.30	0.34	0.88	0.21
110	1.5	2.02	1.17	0.46	0.20	0.32	0.68	0.19
11	1.5	2.98	1.69	0.60	0.12	0.40	0.45	0.23
1	1.5	3.36	1.88	0.90	0.08	0.35	0.28	0.21
108	27	1.14	2.26	0.85	0.05	0.38	0.23	0.20
9	27	0.82	3.36	1.00	0.01	0.38	--	0.05
1	27	0.39	2.87	0.61	0.003	0.21	--	0.03

There are some other interesting results from the high pressure experiments. The nitrogen content of the oil is only slightly less than that at the same heating rate at atmospheric pressure. This indicates that the principal mechanism of coke deposition at high pressure is probably different from that at atmospheric pressure, although our oil characterization is too incomplete yet to be more definitive. In contrast, the sulfur content is approximately independent of heating rate at atmospheric pressure, but is significantly reduced at high pressure, especially at slow heating rates. A similar effect of pressure on nitrogen and sulfur contents was observed by Wise et al. (2). The high pressure oil is also substantially lighter as reflected in density, boiling point distribution and color. In fact, the product from the 27 atm pyrolysis experiments at 1 and 9°C/h is a clear amber rather than the usual opaque brown. A similar observation was made many years ago by McKee (14). Apparently the highly light absorbing chromophores, presumably aromatic heterocycles, are not being formed or are being hydrotreated by the pyrolysis gas. In this regard, we note that the H_2 production is decreased at high pressures.

At the present time, we have just begun our characterization of the liquid product. Analysis by capillary column chromatography has produced some interesting results, a few of which are shown in Figure 2 and in Table IV. Alkene/alkane ratios, as exemplified by 1-dodecene/n-dodecane, decrease with both a decrease in heating rate and an increase in pressure as expected. We have noted previously that ratios involving sums of alkenes and alkanes are nearly independent of heating rate (oil coking) (15). The ratio of phytane to n-octadecane plus 1-octadecene (C_{18}s) is nearly constant. Also, the pristane+enes/phytane ratio is approximately constant although the prist-1-ene/pristane and prist-2-ene/phytane ratios vary dramatically with conditions.

TABLE IV

VALUES OF INDICATOR RATIOS DETERMINED BY CAPILLARY COLUMN GAS CHROMATOGRAPHY

Heating rate (°C/h)	Pressure (atm)	$\frac{\text{1-dodecene}}{\text{n-dodecane}}$	$\frac{\text{phytane}}{C_{18}\text{s}}$	$\frac{\text{pristane+enes}}{\text{phytane}}$	Sterane content
720	1.0	0.84	0.53	2.2	high
110	1.5	0.60	0.47	2.1	medium
11	1.5	0.34	0.45	1.9	medium
1	1.5	0.22	0.43	1.8	medium
108	27	0.21	0.38	1.9	low
9	27	0.09	0.34	1.7	low
1	26	0.03	0.31	1.9	low

However, high temperatures that cause thermal cracking of long-chain hydrocarbons can cause the phytane/C_{18}s ratio to decrease. In Figure 3, we show a reanalysis of old data on shale oil cracking (16). The phytane/C_{18}s ratio decreases because longer chain normal alkanes can crack to n-C_{18}s, but there are no longer-chain isoprenoids to produce phytane. A comparison of

the results in Table IV and Figure 2 indicates that oil yield loss at 27 atm by cracking long-chain hydrocarbons to (primarily) hydrocarbon gases ranges from about 5% at 108°C/h to about 10% at 1°C/h. This is also reflected in the lower boiling point distribution given in Table II. We also note that the high pressure pyrolysis almost completely eliminates the sterane and pentacyclic triterpane content of the oil.

The destruction of steranes and triterpenes caused by the oil cracking may be less in a solid core of material having essentially no initial porosity. The residence time of the biomarker compounds in the reactor would be substantially lower with a smaller initial porosity because they are the first compounds to be evolved (15). The later-evolving products would be affected less by the decreased initial porosity because this grade of shale produces about 25% porosity during oil evolution (17) which would only result in a two-fold change in residence time. The overall yield for a lower porosity reactor might be 5% or so higher at our slowest heating rate and highest pressure.

Finally, we note that high pressure appears to delay evolution (not necessarily generation) of oil. This effect has been previously noted by Noble et al. (3). The temperature for ~99% completion of oil evolution is compared in Table V with that predicted by the kinetic expressions of Campbell et al. (18) and Shih and Sohn (19), both of which were derived at atmospheric pressure. In all cases, a higher temperature is required than calculated. The disagreement is greatest at slow heating rates and high pressures, although the effect of pressure itself appears to be lowest at the slowest heating rates. A more complete comparison of time-dependent oil yield is given in Figure 4 using the kinetic expression of Campbell (18) for the calculated value. Pressure would be expected to affect the oil evolution rate if the rate of evaporation is comparable or slower than the rate of generation.

TABLE V

EXPERIMENTAL (±5°C) AND CALCULATED TEMPERATURES FOR 99% OF OIL EVOLUTION

Heating rate (°C/h)	Pressure (atm)		Calculated	
	1.5	27	Campbell (18)	Sohn (19)
110	465	495	460	465
10	430	455	415	415
1	400	410	380	375

SUMMARY

Rates of oil evolution and oil yields and compositions have been reported for heating rates from 1 to 100°C/hr and pressures up to 27 atm. Pyrolysis occurred in an autogenous atmosphere and generated products were allowed to escape the pyrolysis region continuously. We found that both higher pressures and lower heating rates cause a decrease in oil yield, although the effects are not additive. The lowest oil yield was approximately 72 wt % or 79 vol % of Fischer assay. Lower oil yield is generally accompanied by lower boiling-point distribution, nitrogen content and density and higher H/C ratios. The high-pressure/slow-heating rate oils are a clear amber color instead of the usual opaque brown. We demonstrated the effect of pyrolysis conditions on biological markers and other diagnostic hydrocarbons. Finally, we showed that the rate of oil evolution is retarded by pressure and that existing kinetic expressions for oil evolution overestimate the rate at slow heating rates and high pressures.

ACKNOWLEDGMENTS

We appreciate the design of the apparatus by E. Huss, W. Miller and R. Taylor and the construction and continuing support by J. Taylor and C. Hall. We also thank L. Gregory, J. Clarkson, J. Cupps, C. Otto and R. Ryan for analytical support and R. Taylor for numerous helpful discussions.

Work was performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

APPARATUS FOR PYROLYSIS UP TO 27 ATM

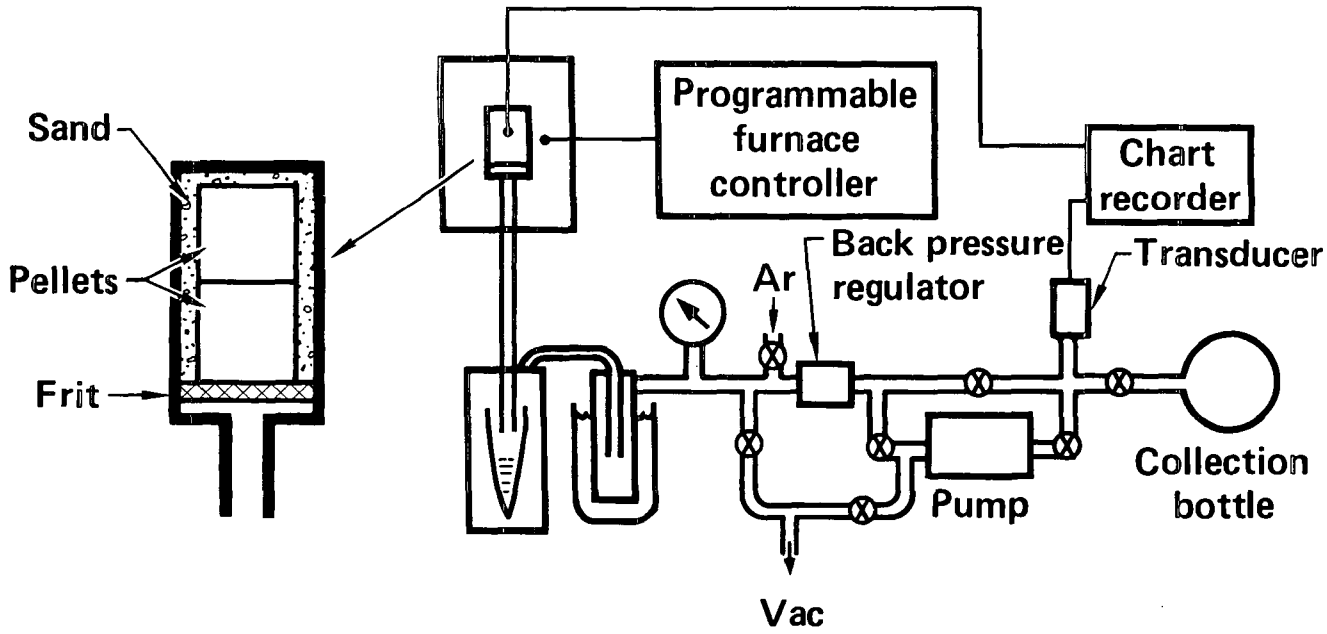

Figure 1. Apparatus for pyrolysis under an autogenous atmosphere.

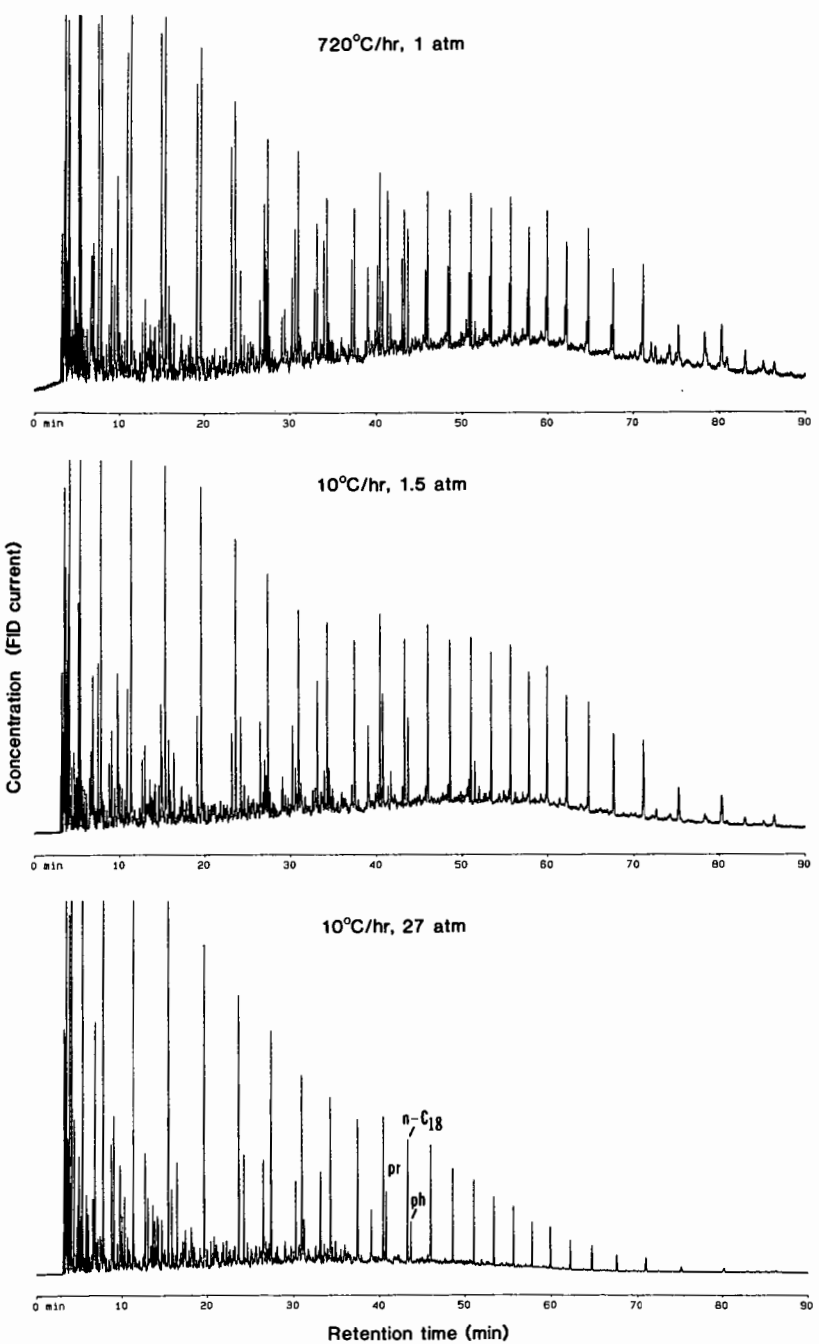

Figure 2. Capillary column gas chromatograms of three oil samples produced during this work. For reference, pristane (pr) phytane (ph) and n-C_{18} are labeled in the bottom chromatogram.

PHYTANE CONCENTRATION IS DECREASED BY CRACKING

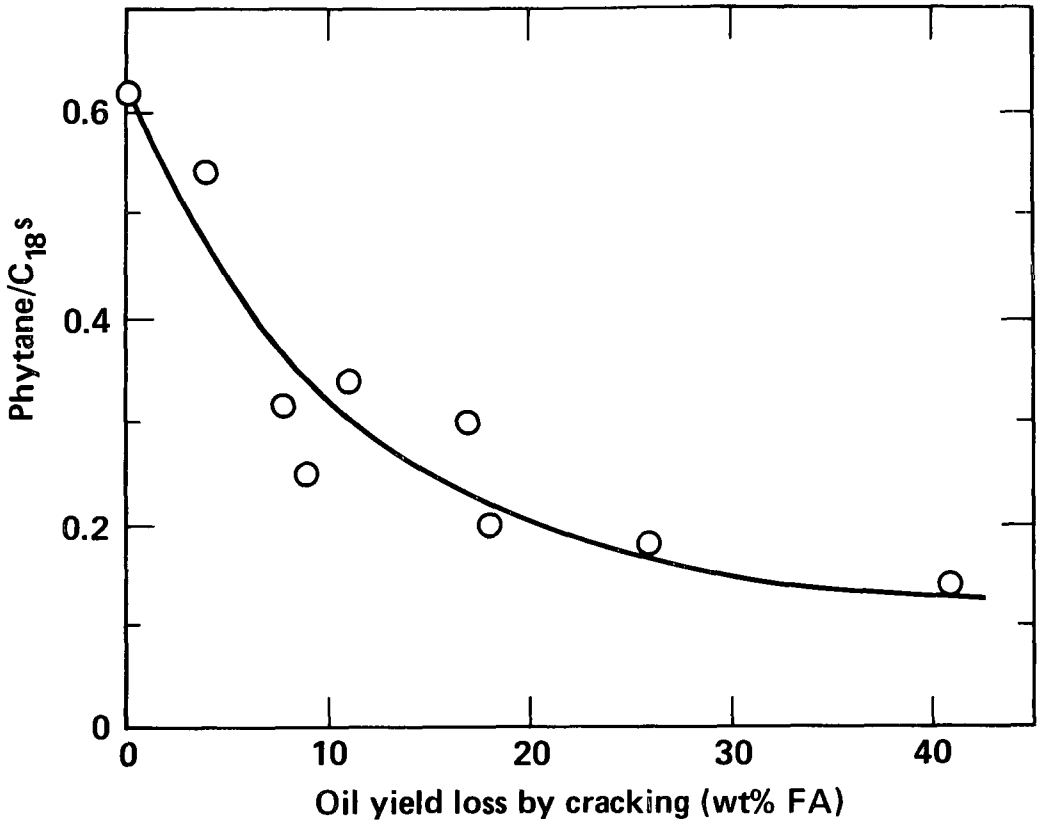

Figure 3. Relationship between phytane content and oil cracking determined from previously reported results (16).

COMPARISON OF MEASURED AND CALCULATED OIL EVOLUTION

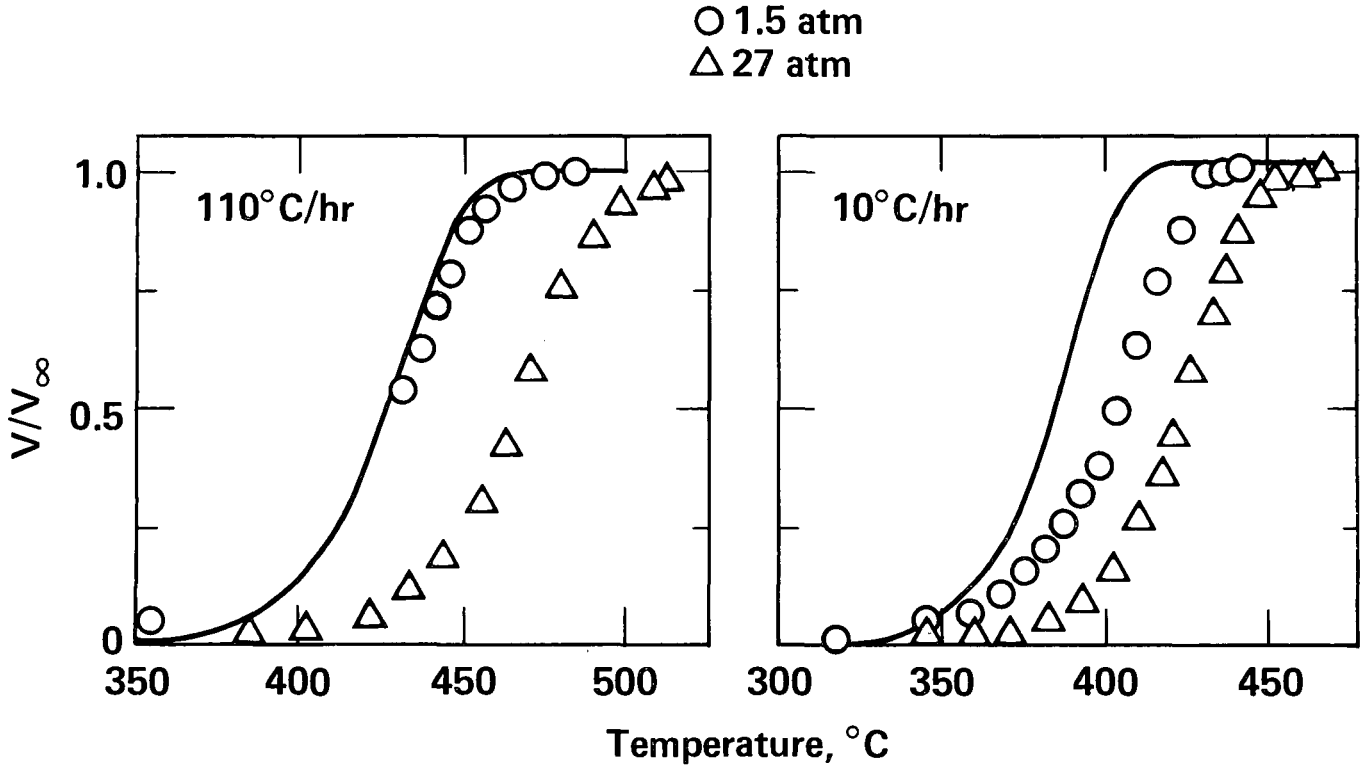

Figure 4. Experimental (points) and calculated (lines) volumes of oil evolved as a function of temperature as the sample is heated at the indicated heating rate.

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